ULTRASONIC VELOCITY IN SUPERCOOLED LIQUIDS

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ABSTRACT. Velocity of ultrasonic waves has been studied over a range of temperatures extending into the supercooled region in five liquids, viz., thymol, phenol, salol, benzophenone, and diphenylamine.

It is observed that the temperature coefficient of velocity $1/c\ (dc/dt)$, does not remain the same on either side of the melting points in thymol and benzophenone. Salol, diphenylamine and benzophenone show a small abrupt change in velocity values as the melting point is crossed. These changes are attributed to possible structural changes encountered during transition from the liquid to the super-cooled state, which must be associated with the corresponding change of adiabatic compressibility. Phenol does not show any discontinuity and the gradient is also the same over the whole range. As phenol is highly hygroscopic it is likely to be mixed with certain amount of water and presumably the presence of water masks the small variation in temperature gradient if any.

INTRODUCTION

The characteristic behaviour of many liquids in passing from the normal state to supercooled state has been studied with respect to the various physical properties such as viscosity (Dodd and Hu,→1949) dielectric constant (Dodd and Roberts, 1950) density (Greenwood and Martin, 1952) specific heat, surface tension (Dodd, 1951) and vapour pressure. Ultrasonic velocity (Barone *et al*., 1957) and absorption (Hunter, 1951, Parthasarathy and Bindal, 19 0) have also been studied to some extent on certain liquids over various ranges of temperatures.

According to Barone, Pisent and Sette some polar liquids which can be easily supercooled show a sudden change of activation energy since viscous flow occures at a temperature near melting point. They attribute this change to some structural variation inside the liquid.

Hunter (1951) worked on menthol and Petra and Cevolain (1951) in salol. Hunter observed a slight variation of temperature co-efficient in menthol but Petra and Cevolain were not able to detect this effect in salol.

Subsequently, Barone, Pisent and Sette (1957) have investigated, menthol diphenyl ether, *m*-chloronitrobenzene and salol in the normal and supercooled regions. They have discussed the results on the basis of viscosity measurement

and explained that the structural variation, which might be responsible for the variation in temperature co-efficient in the two states of liquid are mainly due to formation of molecular associations

The present work was undertaken to study some more liquids and to investigate their behaviour with respect to ultrasonic propagation in the temperature range of 30°C to 70°C, the melting point of the liquids in question being in the region of 50°C With the help of a precision interferometer the ultrasonic velocity was measured in salol, thymol, benzophenone, diphenylamine and phenol.

EXPERIMENTAL

The work under report was done at a frequency of 6 Mcs The r f. generator used consisted of 2 Mcs crystal controlled oscillator in the form of a modified Pierce oscillator This was followed by an amplifier tripler stage giving 6 Mcs The r f output was fed to the load crystal fixed at the bottom of the interferometer through a condenser coupling The H T current to the output tube was fed through a bridge net-work including a microammeter in such a way that changes in the plate current could be easily observed on the microammeter

A precision interferometer was used for finding out the velocity at different temperatures by measuring the half wave-length in the liquid under test by shifting the reflector plate with the help of a micrometer screw

If sound waves proceeding from a vibrating quartz are incident on plane reflector parallel to the source a standing wave pattern is obtained The plate current of the output tube registers a change depending on the reaction on the transducer produced by a reflected wave This reaction is maximum when the reflected wave returns 180° out of phase with the out going wave in which case the plate current shows a maximum dip As the position of the reflecting plate is further changed the reaction on the generator passes through a maximum for each $\lambda/2$ path difference of sound waves corresponding to movement of the reflector. The reflector movements can be very accurately read with the help of micrometer screw driving it In the electric circuit, the bridge network is so adjusted for maximum sensitivity that the dips in the current can be easily counted as the reflector plate is moved. The total distance travelled by the reflector divided by the number of dips gives the value of half the wave length Knowing the frequency of the oscillator the velocity can be calculated

For the measurement of the velocity at different temperatures, water, from a thermostatically controlled bath was circulated around the liquid under experiment in the interferometer with the help of a centrifugal pump and the temperature was recorded with the help of 1/10°C thermometer, the temperature was constant within 0 1°C

The arrangement gives .05% as the accuracy in velocity measurement.

RESULTS AND DISCUSSION

The results obtained in salol, thymol, benzophenone, diphenylamine and phenol are given in Figs. 1, 2, 3, 4 and 5 respectively. They have also been placed in a tabular form for comparison.

It is noticed from the above results that in phenol (Figs 5) there is no change in ultrasonic velocity as the temperature is reduced below the melting point into the supercooled region. The reason for this may be due to its hygroscopic nature, it is likely to be mixed with certain amount of water. Presumably the presence of this water masks the small variation in temperature gradient if any in phenol

TABLE I

Comparison of velocity (M/sec) in different liquids at different temperatures

S No.	Temp. °C	Salol m.p. 42°C	Thymol m.p 51.5°C	Benzophenone m.p 48°C	Diphenylamine m.p 54°C	Phenol m.p 41°C
1	30	1463 00	1406.00	1544.00	1622 00	1485 00
2	33	1453 50	1396 00	1535 00	1611 00	1475 50
3	36	1444 00	1387 00	1526 00	1600 00	1466.00
4	39	1434.00	1378 00	1517.00	1589 00	1457 00
5	42	m.p.	1368.00	1508 00	1578 00	1448 00
6	45	1412.00	1359 00	1499 00	1567 00	1439 00
7	48	1402.50	1350.00	m p.	1556 00	1429.50
8	51	1393 00	1240 75	1477 00	1545 00	1420 00
9	54	1383.50	1330 00	1465 50	m p.	1411 00
10	57	1374 00	1320 00	1454 00	1417 75	1401 75
11	60	1364.75	1310.00	1442.50	1507 00	1392 25
12	63	1355 00	1300 00	1431 00	1496.00	1383.00
13	66	1346 75	1290.00	1419.25	1486 00	1374 00
14	69	1337 00	1280 00	1407 75	1475 00	1364.75
15	72	1228 00	1270 00	1396 50	1464 75	1355.50

In the case of thymol (Fig. 2) it is noticed that there is no appreciable abrupt change in the velocity near the melting point but the temperature co-efficient of velocity is different on either side. Benzophenone, (Fig. 3) salol (Fig.1), and diphenylamine (Fig 4) show a sudden change in velocity. In salol (Fig. 1) the change is about 11 meter as the temperature is lowered by about 2.5°C in the

neighbourhood of the melting point whereas the normal variation of velocity for 2.5°C change of temperature is found to be about 7 m only.

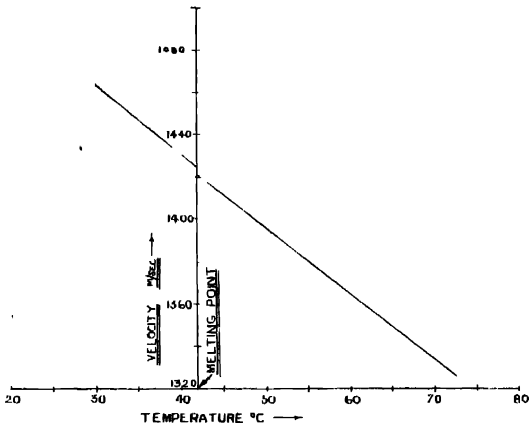

Fig. 1. Ultrasonic velocity in phenyl salicylate (salol).

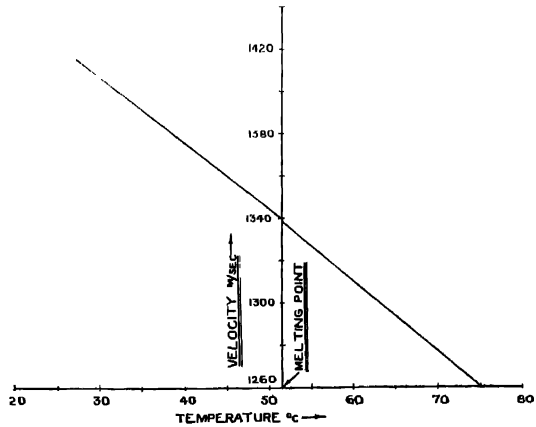

Fig. 2. Ultrasonic velocity in thymol.

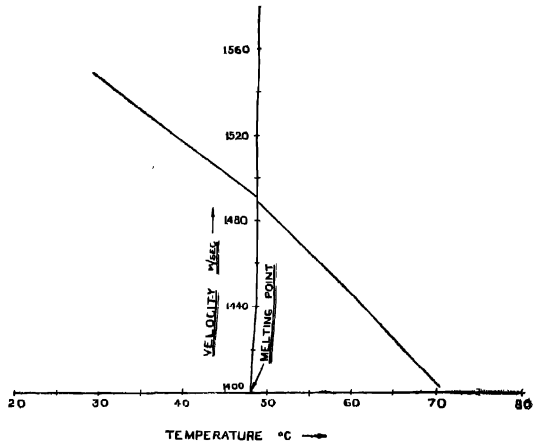

Fig 3. Ultrasonic velocity in benzophenone

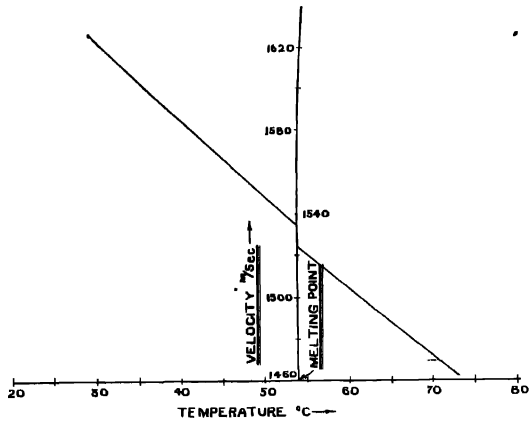

Fig. 4. Ultrasonic velocity in diphenylamine.

The curve obtained in salol (Fig 1) in the present case does not agree with the curve obtained by Barone and Pisent (1957). They have reported that in the neighbourhood of the melting point, the velocity is changing from higher to lower values as the temperature is lowered to supercooled region whereas in the

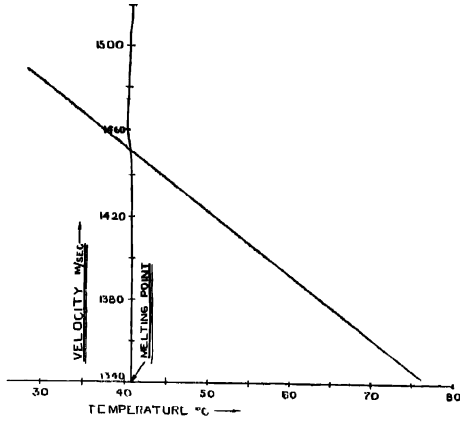

Fig 5 Ultrasonic velocity in carbolic acid (phenol)

other liquids studied by them give the reverse order. In the work under report not only benzophenone and diphenylamine but also salol show an abrupt increase of velocity as the temperature is lowered to cross the melting point. Presently, it may be explained that the variation in the values in the two regions may be due to structural changes which take place in liquid from normal to supercooled state. Any change in the structure is likely to be associated with a corresponding change of adiabatic compressibility. Dodd (1949) working on measurement of densities of various supercooled liquids observed no detectable change in the temperature-co-efficient of density. This again indicates that the adiabatic compressibility must show an abrupt change at the melting point of the liquids. In the present case if the densities of these liquids are also measured over a similar range of temperature extending into the supercooled region it would be possible to calculate the actual adiabatic compressibility from velocity data already obtained. Work on other lines is in progress

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